

# Amperometric Titration of Nornicotine

G. O. WILLITS AND CONSTANTINE RICCIUTI

Regional Research Laboratory, Philadelphia 18, Pa.

NORNICOTINE can be determined by quantitative precipitation with silicotungstic acid by a method similar to that used for nicotine (1). Bowen and Barthel (2) determined nicotine and nornicotine in the steam distillate of tobacco from the difference in the weights of the total alkaloid-silicotungstates before and after the destruction of nornicotine with nitrous acid. Larson and Haag (3) determined nornicotine by forming a colored complex with cyanogen bromide and then measuring its absorption intensity in a spectrophotometer.

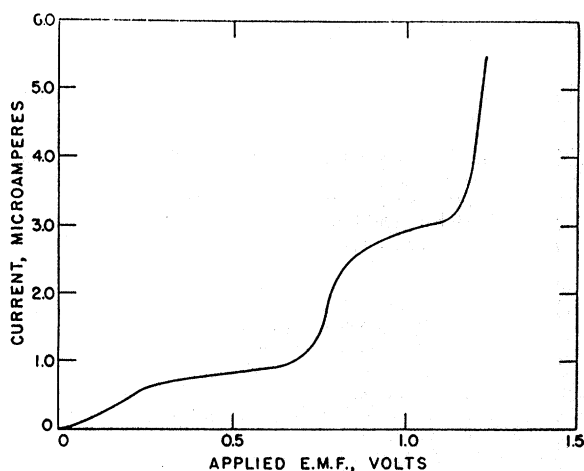


Figure 1. Polarogram of Nornicotine

For some time amperometric titration methods have been successfully used for inorganic analyses (5-7, 11-13), and recently the method has been applied to organic compounds (3, 4, 10). Two prerequisites of the amperometric titration method are: that the substance being analyzed or the titrant used should be polarographically reducible, and that the substance being measured be removed from solution as either a precipitate or a nonreducible complex. The titration of nornicotine with silicotungstic acid fulfills these conditions. Both nornicotine and silicotungstic acid are reduced polarographically and the nornicotine is quantitatively precipitated by silicotungstic acid. The amperometric method should therefore be applicable to the determination of nornicotine (in the absence of nicotine) and should also provide quantitative information on the mechanism of formation of the nornicotine-silicotungstate precipitate.

## EXPERIMENTAL

A continuous reading Sargent Model XX polarograph and a Lingane H-cell (9) with a saturated calomel electrode as reference electrode were used. The cell was covered with a plastic cap with openings for introducing the buret tip and capillary. With the capillary in place, oxygen-free nitrogen was bubbled through the solution for 2 minutes after each addition of titrant to remove any dissolved oxygen which would produce an interfering polarographic wave. In addition to the nornicotine, the electrolyte solution contained 0.1 mole of lithium chloride and 0.1 mole of hydrochloric acid per liter as an indifferent or supporting electrolyte.

The applied potential of -0.90 volt used in the amperometric titration of nornicotine was established from a polarogram of a  $2.879 \times 10^{-3} M$  nornicotine with 0.1 M hydrochloric acid and 0.1 M lithium chloride as supporting electrolytes. The nornicotine polarogram was recorded in a cell held at 5°C., as at higher temperatures the wave was not well defined.

As shown in Figure 1, nornicotine had a half-wave potential of -0.78 volt referred to a standard calomel electrode, and the flat portion of its wave was at -0.90 volt. Silicotungstic acid in the same electrolytic medium also has the flat portion of its reduction wave at -0.90 volt, as shown in Figure 2.

Figure 3 shows a typical amperometric titration plot obtained for 50 ml. of  $1.440 \times 10^{-3} M$  nornicotine in 0.1 M hydrochloric acid and 0.1 M lithium chloride titrated with  $6.197 \times 10^{-3} M$  silicotungstic acid in increments at 3-minute intervals. The points were obtained by plotting the wave height in millimeters against volume of titrant added. Repeated trials with the nornicotine-silicotungstate titration, in which a relatively short period (3 minutes) elapsed between additions of the titrant always showed a similar but erratic pattern of points which indicated the formation of an unstable precipitate.

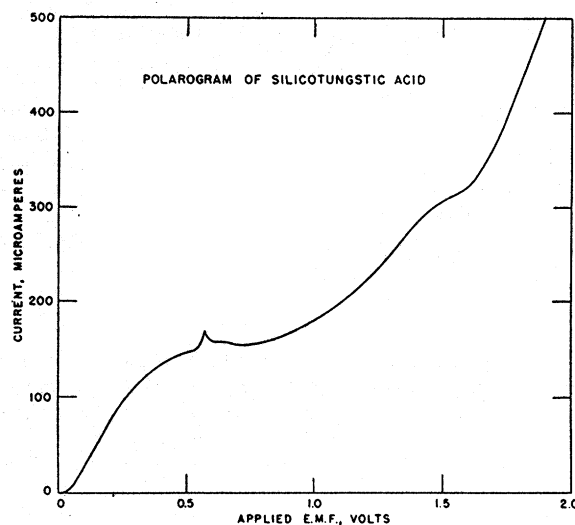


Figure 2. Polarogram of Silicotungstic Acid

Figure 4 shows a typical amperometric titration using 50 ml. of  $2.231 \times 10^{-3} M$  nornicotine in the same electrolyte solution to which portions of  $4.892 \times 10^{-3} M$  silicotungstic acid were added at 15-minute intervals. The intersection point of the projected straight lines was 11.35 ml. of added silicotungstic acid. In this case the molar ratio was 2 to 1, as the calculated volume of silicotungstic acid required for this ratio was 11.40 ml. The anomaly

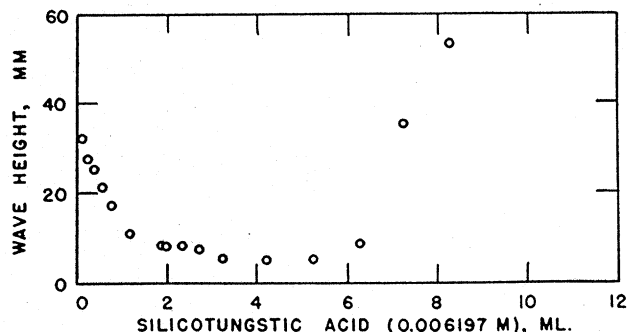


Figure 3. Typical Amperometric Titration Plot of Nornicotine

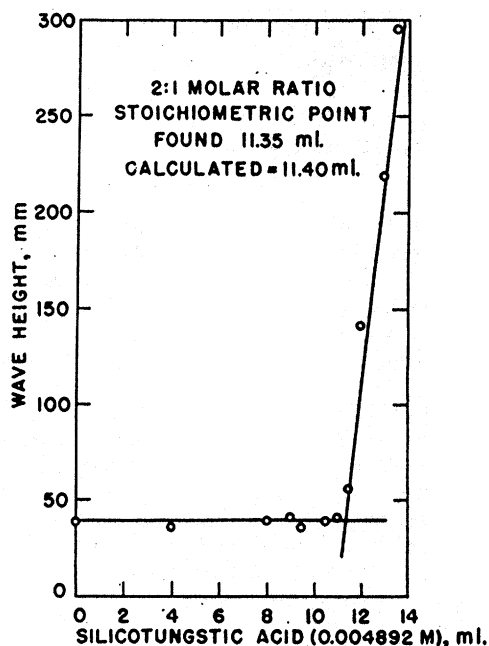


Figure 4. Amperometric Titration Plot of Nornicotine

lous nonreducibility of the nornicotine solution when titrated under the "slow" conditions is not readily explained. It is not due to a pH effect, as the pH remains constant throughout the titration. The horizontal, linear segment of Figure 4 is above the zero ordinate because no correction has been made for residual current, 40 mm. or 0.8 microampere. Such a correction would lower this line to the zero ordinate.

#### DISCUSSION

The amperometric curves for nornicotine titrated with silicotungstic acid showed that the composition of the precipitate depended upon the time allowed for equilibrium. When the titra-

tion was conducted rapidly by adding the silicotungstic acid at 3-minute intervals, an unstable precipitate was formed. However, when the same titration was conducted at a slower rate—i.e., adding the acid at 15-minute intervals—the stable precipitate with a 2 to 1 molar ratio of nornicotine to silicotungstic acid was obtained. The points for the slower titration were less scattered than those for the rapid one. The points were even less erratic when the titration was conducted at 5° C. than at higher temperatures. The close agreement between the values obtained from eight separate amperometric titrations and the calculated values indicates that this method can be used to determine concentrations of 2 to 3 mg. of nornicotine per ml. with a probable error of  $\pm 2\%$  of the amount of nornicotine present.

#### ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of Abner Eisner, who prepared the samples of nornicotine used in these studies.

#### LITERATURE CITED

- (1) Association of Official Agricultural Chemists, "Official and Tentative Methods of Analysis," 6th ed., p. 74, par. 6.103-9, 1945.
- (2) Bowen, C. V., and Barthel, W. F., *IND. ENG. CHEM., ANAL. ED.*, 15, 740 (1943).
- (3) Conn, J. B., *ANAL. CHEM.*, 20, 585 (1948).
- (4) Elofson, R. M., and Mecherly, P. A., *Ibid.*, 21, 565 (1949).
- (5) Kolthoff, I. M., and Langer, A., *J. Am. Chem. Soc.*, 62, 211 (1940).
- (6) *Ibid.*, p. 3172.
- (7) Kolthoff, I. M., and Lingane, J. J., "Polarography," New York, Interscience Publishers, 1941.
- (8) Larson, P. S., and Haag, H. B., *IND. ENG. CHEM., ANAL. ED.*, 16, 86 (1944).
- (9) Lingane, J. J., and Laitinen, H. A., *Ibid.*, 11, 504 (1939).
- (10) Smith, L. I., Kolthoff, I. M., and Spillane, L. J., *J. Am. Chem. Soc.*, 64, 646 (1942).
- (11) Spalenka, J., *Collection Czechoslov. Chem. Commun.*, 11, 146 (1939).
- (12) Stock, J. T., *Analyst*, 72, 291 (1947).
- (13) Thanheiser, J., and Willems, J., *Arch. Eisenhüttenw.*, 13, 73 (1939).